

On the Refraction and Dispersion of Gaseous Nitrogen Peroxide.

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The study of the refraction and dispersion of gaseous nitrogen peroxide (NO_2 , N_2O_4) is specially interesting, owing to the opportunity it affords for observing the changes which accompany the polymerisation of the molecule. No previous determinations are recorded in the usual books of reference.

Preparation.

The gas which we used was prepared by heating pure lead nitrate, which had previously been ground to fine powder and heated for two hours to 150°C . to expel moisture. It was condensed in a bulb, and quantities of about a cubic centimetre of the liquid were sealed off in glass tubes which were broken *in vacuo* in a dry bulb containing P_2O_5 . Taps were usually lubricated with metaphosphoric acid, but in some cases with a mixture of pure paraffin and vaseline, which was not appreciably attacked by the gas.

Apparatus and Procedure.

For the determination of refractive indices Jamin's refractometer was used. The bulb containing the liquid NO_2 was connected with the refractometer tube by a tap. Another tap connected with a manometer, consisting of two U-tubes in series, the first containing oil and the second mercury. A long capillary separated the oil from the tap which led to the NO_2 .

In a measurement of the refraction the liquid NO_2 was first cooled to -80°C ., at which temperature its vapour pressure is negligible, and the whole apparatus was evacuated with a Töpler pump, through tubes containing soda-lime and potash and P_2O_5 , till the difference of pressure shown by the manometer corresponded with the barometric height.

The manometer tap was then closed and the liquid allowed to warm, while the observer counted the interference bands which passed the cross-wire as the vapour flowed into the refractometer tube. When a convenient number had passed, the tap connecting the bulb of NO_2 was closed, and dry air was admitted into the manometer till the pressure nearly equalled that of the nitrogen peroxide. The manometer tap was then opened, and the difference between the pressure of the atmosphere and that of the gas was read.

The barometric height was again taken, the temperature observed, and the number of bands noted.

The density of the gas present in the refractometer tube was determined by means of a density bulb connected with it in parallel, and immersed in the same water-bath.

Light.

Owing to the strong absorption of the vapour it was found impossible to use the mercury green line ($\lambda = 5460$) for measurements of refraction. For this purpose we used red light ($\lambda = 6438$) obtained by means of a fixed-deviation spectroscope, fitted with an adjustable slit at the eye end, which sifted out a band of light not exceeding 10 Å.U. in width. Even with this red light the maximum number of bands which could be counted when the vapour contained 96 per cent. of NO_2 was only about 80, so that great accuracy was not attainable.

Reduction of Observations.

Our object is to compare the refractive and dispersive powers of the molecules of NO_2 and N_2O_4 respectively, and their relation to those of nitrogen and oxygen. It is, therefore, necessary to reduce the refractivities experimentally observed at various temperatures and pressures to the same standard conditions as those under which the refractivities of the permanent gases are usually expressed. These are, of course, that the temperature and pressure of the gas should be 0°C. and 760 mm. But in dealing with substances which are not perfect gases, it is desirable to substitute for these conditions the real standard which they are meant to define, viz., that the number of molecules of the gas present in unit volume should equal the number of molecules present in unit volume of a permanent gas, *e.g.* oxygen, at 0°C. and 760 mm. pressure.

In the present case the pressure and temperature of the gas were observed, and it was assumed, for the purpose of the reduction, that each constituent (*i.e.* NO_2 and N_2O_4) behaved as a perfect gas, and that the mixture remained of the same composition. Upon these assumptions the reduced refractivity, which we shall denote by $(\mu_\lambda - 1)_{0.76}$, is given by

$$(\mu_\lambda - 1)_{0.76} = \frac{N\lambda}{L} \frac{t}{273} \frac{76}{p},$$

where N is the number of interference bands, L the length of the tube, t and p the temperature and pressure of the experiment.

The observed density* of the gas was reduced in the same manner. If d denotes the observed density (grammes per litre) and D the reduced density,

$$D = d \frac{t}{273} \frac{76}{p}.$$

The standard density for each constituent was obtained from the following figures:—

						Grammes.
Weight of 1 litre of nitrogen at 0° C. and 76 cm.						1.25718
" $\frac{1}{2}$ " " "						0.62859
" 1 " oxygen "						1.42952
Hence " 1 " NO ₂ "						2.05811
and " 1 " N ₂ O ₄ "						4.11622

We have thus obtained a reduced refractivity and a reduced density. The former expresses the refractivity which would be given at 0° C. by a gaseous mixture in which the proportions of molecules of NO₂ and N₂O₄ were those which exist at the temperature and pressure of the experiment, and for which the density was such that the number of molecules present per cubic centimetre was equal to the number present in unit volume of oxygen at 0° C. and 760. The latter gives us the weight of unit volume of the gaseous mixture under the same conditions.

Assuming the additive law to hold good for the gaseous mixture, it is evident that if we plot the reduced refractivities against the reduced densities, we should obtain a straight line. The values of the reduced refractivities which correspond with the standard densities of NO₂ and N₂O₄ given above will be the refractivities of NO₂ and N₂O₄ under the standard conditions.

Table I gives the results of ten experiments on the refraction.

* It may be asked why we did not use the observations of E. and L. Natanson on the connection between the density, temperature and pressure of NO₂ ('Wied. Ann.,' vol. 24, p. 445, and vol. 27, p. 606). These were determined from observations at nine temperatures nearly all above 20° C., and at the low temperatures and pressures which it was necessary for us to use in order to obtain a large percentage of N₂O₄, the discrepancies between their observations and the values calculated from Willard Gibbs' formula are so great that it was impossible to use them for the calculation of the density at intermediate temperatures and pressures.

Schreber ('Zeit. Phys. Chem.,' 1897, vol. 24, p. 660) has analysed the observations of the brothers Natanson, and gives a formula from which the dissociation constant can be calculated at any temperature and pressure. Our first series of experiments was based on the use of this formula, but after three months' work it was found that it, too, is untrustworthy at low temperatures.

Table I.—Refractivity of Gaseous Nitrogen Peroxide ($\lambda = 6438$).

No. of expt.	Length of tubes.	Temperature (absolute).	Pressure.	No. of bands for $\lambda = 6438$.	Refractivity $(\mu-1)10^7$.		Density.	
					Experimental $\left(\frac{N\lambda}{L}\right)$.	Reduced $\left(\frac{N\lambda}{L} \cdot \frac{t}{273} \cdot \frac{76}{p}\right)$.	Experimental. $d = \frac{\text{gram.}}{\text{litre}}$.	Reduced. $D = \frac{\text{gram.}}{\text{litre}} \cdot \frac{t}{273} \cdot \frac{76}{p}$.
	mm.		mm.					
5	197·78	273	180·4	71·35	2323	9785	0·8625	3·634
8	197·78	273	176·9	69·7	2269	9748	0·8453	3·632
3	197·78	279	190·9	71·6	2331	9483	0·8663	3·523
4	197·78	283·6	187·35	66·6	2168	9139	0·8086	3·408
1	197·78	288·9	174·3	57·45	1870	8629	0·7029	3·240
9	197·78	299·6	237·9	70·0	2279	7990	0·8660	3·037
6	197·78	303	196·5	51·7	1683	7225	0·6455	2·771
7	197·78	311	189·5	47·25	1538	7027	0·5944	2·716
11	997·86	308·9	55·3	60·4	389·7	6059	0·1522	2·367
12	997·86	342·9	61·15	49·7	221·2	5006	0·1314	2·052

In fig. 1 the values for the reduced refractivity are plotted against the corresponding values for the reduced density.*

The points fall on a straight line which cuts the ordinate whose abscissa is 2·0581 at the point 508·7, and the ordinate whose abscissa is 4·1162 at the point 1123. The constants, calculated by the method of least squares, give the following equation to this line:—

$$10^7(\mu-1)_{0.76} = 2983.4 D - 1053.3.$$

* It is, perhaps, not obvious why we should not obtain a similar straight line by plotting the experimental values of the refractivity and density instead of the reduced, since the latter are both derived from the former by multiplying by the same factor. But this is not so.

In any one gaseous mixture let there be n_1 molecules of NO_2 and n_2 of N_2O_4 . Let the refractivities of one molecule of NO_2 and one molecule of N_2O_4 be denoted by (μ_1-1) and (μ_2-1) respectively, and that of the mixture by $(\mu_{12}-1)$; and let the molecular weights of the two constituents be M_1, M_2 .

$$\text{We have} \quad (\mu_{12}-1) = n_1(\mu_1-1) + n_2(\mu_2-1), \quad i$$

and, assuming the perfect gas law for each constituent,

$$p = (n_1 + n_2) R t, \quad i$$

also

$$d = n_1 M_1 + n_2 M_2,$$

$$\text{whence} \quad (\mu_{12}-1) = \frac{p}{R t} \frac{[(\mu_1-1) M_2 - (\mu_2-1) M_1] + d(\mu_2-\mu_1)}{M_2 - M_1}.$$

Multiplying by $\frac{t}{p}$ we have

$$(\mu_{12}-1) \frac{t}{p} = \frac{1}{R(M_2 - M_1)} [(\mu_1-1) M_2 - (\mu_2-1) M_1] + \frac{d t (\mu_2 - \mu_1)}{p (M_2 - M_1)},$$

a linear equation between the reduced refractivity and reduced density.

The discrepancies between the calculated and observed values of the refractivity are all less than 0.35 per cent., except in the last two experi-

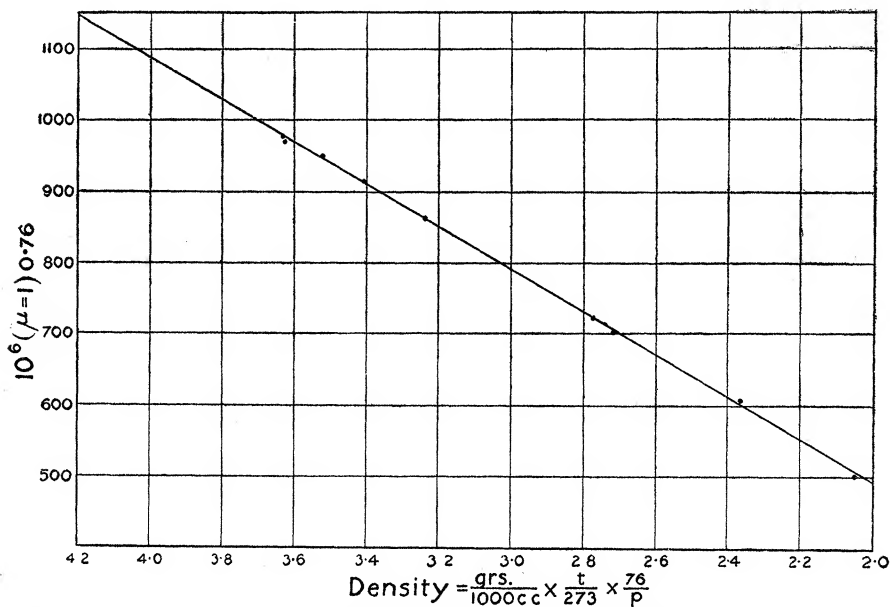


FIG. 1.—Reduced refractivity of nitrogen peroxide plotted against reduced density.

ments, where they are +0.85 and -1.2 respectively. This was to be expected, owing to the low pressure and high temperature of the experiments, which increases the difficulty of determining the density.

Hence, finally, we obtain as the reduced refractivity of pure NO_2 for $\lambda = 6438$

$$10^7 (\mu - 1)_{0.76} = 0.0005087,$$

and for pure N_2O_4 $10^7 (\mu - 1)_{0.76} = 0.001123.$

It thus appears that the refractivity of a molecule of N_2O_4 exceeds that of two molecules of NO_2 by about $10\frac{1}{2}$ per cent.

In order to check this result we tried the experiment of operating with a constant density of gas at different temperatures. The gas was admitted to the tube in the usual way, and the pressure, temperature, and bands read. The refractometer tube was then sealed off with as short a side tube as possible, and the tubes were heated and cooled in a water-bath, while the variation of the position of the bands was observed. The results were as follows :—

Temperature.	Pressure.	Bands.
274·1	37·74	62·45
290	Not observed	60·8
303	„	60·2
331·5	„	57·4
344	„	57·3

As the temperature was raised the proportion of molecules of NO_2 increased, while the density of the gas remained constant. The diminution of the retardation of light under these circumstances, which is shown by the retrogression of the bands, proves that the refractivity per molecule of NO_2 is less than that of N_2O_4 . The rate of diminution is rather faster than we should expect from the results of the main experiment; but the accuracy of this subsidiary form of experiment is seriously affected by “drift” or “end effects” owing to the changes of temperature, and the weight to be attributed to it, as a quantitative experiment, is small.

Relation to Refractivities of Nitrogen and Oxygen.

We have recently shown that the refractivities of ammonia, nitric oxide and nitrous oxide are greater than the sum of the refractivities of the elements which compose them by 3·6, 3, and 16·3 per cent. respectively.*

Nitrogen peroxide exhibits the same phenomenon. The additive value for NO_2 is found from

$$(\mu-1)_{\text{N}_2} = 0\cdot000299.$$

Half of this is

$$0\cdot0001495,$$

and

$$(\mu-1)_{\text{O}_2} = 0\cdot000271.$$

The sum is

$$0\cdot0004205,$$

while the experimental value is 0·000509, an increase of 21 per cent.

DISPERSION.

Procedure.

Measurements of the dispersion are limited, by the absorption, to the red and green, and even in this region trustworthy values would be difficult to obtain were it not for the enormous dispersive power of the molecule of NO_2 . In order to trace the shape of the dispersion curve as it passes through the absorption bands it was necessary to abandon the monochromatic sources of light which are available when a gas is transparent

* ‘Phil. Mag.’ April, 1913, p. 592.

to the whole spectrum, and to do the best which is possible with a narrow section of the spectrum of white light. In this case the source was a Nernst lamp. The fixed-deviation spectroscope was fitted with an adjustable slit at the eye end, and the two slits were narrowed till the beam which passed through the second slit did not exceed 10 Å.U. in breadth. The apparatus was evacuated and the optical paths of the two beams equalised by means of the compensator, so that no movement was seen in the position of the interference bands as the light was continuously changed from λ 6708 to λ 5461. Gas was now admitted till a convenient number of bands (λ 6438) had passed, when the supply was cut off. The compensator was then altered till the same number of bands had passed in the opposite direction. If the wave-length drum is now rotated any change in the position of the band is due to the difference of dispersive powers of glass and gas.*

Three sets of experiments were made; the first, at the lowest temperature and highest pressure which could conveniently be used, so as to obtain the greatest proportion of molecules of N_2O_4 . The reduced density of this mixture was about 3.63, and the proportion of molecules of N_2O_4 present was 76.5 per 100 molecules.

At an intermediate temperature and pressure a single experiment was made on gas containing 48 per cent. of molecules of N_2O_4 .

The third set was made at the highest temperature and lowest pressure convenient, on gas containing approximately 4 per cent. of molecules of N_2O_4 and 96 per cent. of NO_2 .

The results are shown graphically in fig. 2 (1, 2, 3).

In the first set of experiments, in which the proportion of NO_2 was small, the curve could be traced throughout its whole length as far as $\lambda = 5500$. It is comparatively smooth, but shows clearly the characteristic rise and relative fall on passing through each region of absorption.

In fig. 2 (2) is shown the curve obtained with 52 per cent. NO_2 , but the final density of the gas was so great that much light was absorbed, and

* The compensator was of special design and retards light of all wave-lengths equally except so far as dispersion affects them. It consisted of two pairs of wedge-shaped pieces of glass, with their thick ends opposed, mounted vertically in a metal frame with their exterior surfaces at right angles to the beam of light.

Three of the wedges are fixed. The fourth is movable vertically by means of a screw, and is mounted so that the distance between the interior surfaces remains constant. Each of the two beams of light passes through one pair of wedges, which are optically equivalent to a plane parallel sheet of glass. By screwing the movable wedge up or down, the path of one of the two beams is accelerated or retarded, and all wave-lengths equally, except so far as dispersion affects them.

only six points on the curve could be obtained, intermediate parts of the spectrum being obliterated.

Fig. 2 (3) gives the curve obtained from the third set of experiments, when 96 per cent. of NO_2 was present. It shows the increased size of the humps

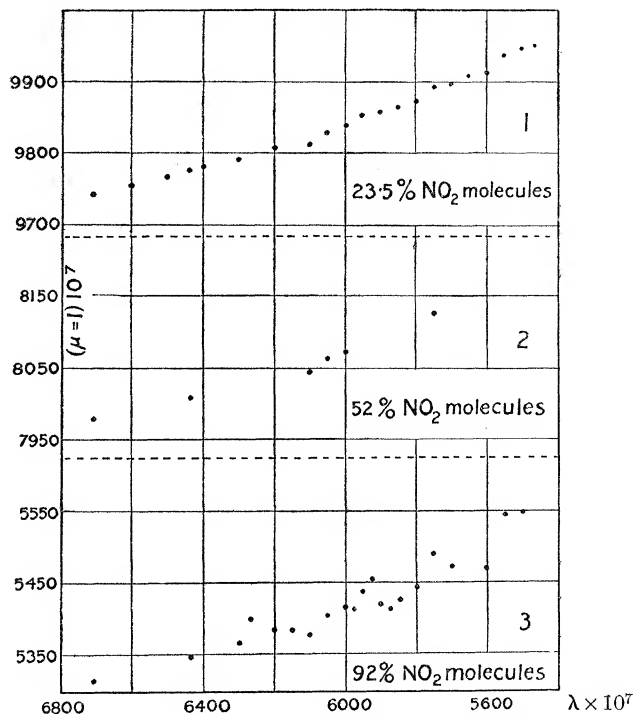


FIG. 2.—Dispersion of nitrogen peroxide.

on the curve due to the increased percentage of NO_2 , and gives a fair idea of the position of their maxima and minima. But farther than this the accuracy of this series cannot be trusted. In order to obtain readings between $\lambda \lambda$ 6000 and 5600, it was necessary to reduce the number of bands to 17, and even to 13, and, under these conditions, an error of $1/30$ of an interference band was equivalent to an error of 0.004 in the value of the refractivity.

In the figure the three curves have about the same inclination to the horizontal. But, since the refractivity diminishes as we pass from (1) to (3), the dispersive power $(\mu_1 - \mu_2)/(\mu_1 - 1)$ increases in the same order and proportion.

Remarks.

It is well known that, with sufficient dispersion, and at low temperatures, the absorption bands of NO_2 are seen to consist of fine lines, which blend into a band as the temperature is raised,* and, no doubt, if it were possible to trace our dispersion curve from line to line, a series of small maxima would be shown. Our apparatus is not capable of indicating these microscopic changes, but only records the general effect in passing through a region of absorption.

The most interesting question raised by these observations is the cause of the increase of refractivity which accompanies polymerisation, coupled with the decrease of dispersive power. It is much to be desired that measurements of the refractivity should be supplemented by accurate observations of the position of the absorption bands in the infra-red and ultra-violet for each constituent separately. So far as we can discover, no one has attempted this. Hartley† records that the gas is transparent between $\lambda\lambda$ 321 and 238, but this appears to be all that is known.

We are much indebted to the Royal Society for a grant in aid of this work.

Summary.

The results given above may be summarised as follows:—

1. The refractivity of pure NO_2 for $\lambda = 6438$, reduced to standard conditions by the formula $(\mu-1)_{0.76} = \frac{N\lambda}{L} \frac{t}{273} \frac{76}{p}$ is approximately 0.000509. That of pure N_2O_4 is 0.001123, so that the effect of polymerisation is to increase the refractivity by about $10\frac{1}{2}$ per cent.
2. The refractivity of a molecule of NO_2 is greater than those of the elements of which it is composed by 21 per cent.
3. The dispersive power of a molecule of NO_2 in the red and green is considerably greater than that of a molecule of N_2O_4 .

* Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 46, p. 222.

† Hartley, 'Chem. Soc. Journ.,' 1881, vol. 39, p. 111.